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GEOCHEMICAL INTERACTIONS OF HEAVY METALS IN SOUTHEASTERN SALT MARSH ENVIRONMENTS

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The results provide a base for future evaluation of the rates of inputs of the metals studied and their existing concentrations in the water and sediment column of salt marsh estuaries. The interactions of metals with organic matter in rivers and estuaries and their effect on transport and fate are discussed. The effects of processes such as flocculation, precipitation, adsorption, and desorption from particles in estuaries are evaluated. The distribution and rate of accumulation of Hg, Cd and other metals in salt marsh sediments are compared to their inputs to determine the amount of these metals that ultimately reach coastal littoral waters. And finally, the residence time of Hg and Cd in coastal littoral waters is estimated from their input rates and concentrations.

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This report summarizes the results of a three year study of the transport, fate, and geochemical interactions of mercury, cadmium, and other inorganic pollutants in the southeastern coastal littoral-salt marsh environment. The general objectives of the study were to determine: 1) the rate of input of these materials to salt marsh estuaries, 2) the geochemical interaction they experience there and, 3) their ultimate fate in coastal littoral waters.

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SECTION I

CONCLUSIONS

The conclusions from this study relate specifically to southeastern United States rivers, salt marsh estuaries and coastal areas. It is likely that many of the conclusions apply to other areas as well; however, this point must be made to insure that unique characteristics of the environments studied are not assumed to be universally common.

Generally the conclusions of this report are of the greatest practical value in evaluating the present and potential impact of man's activities on water quality in the southeastern coastal littoral-salt marsh environment. The principal conclusions are as follows:

1. Southeastern rivers are similar in their concentrations of dissolved mercury and cadmium with mean values of 0.04 to 0.07 and 0.3 and 1.0 µg/l, respectively. In this regard heavily industrialized rivers do not differ from those that are undeveloped. This suggests that metal inputs are not reflected in the water column but are probably evident in sediments. Greatest effects are more likely to be observed in the immediate area of the input.

2. The high levels of dissolved and particulate organic matter in southeastern rivers can influence the fate of metal pollutants. This is especially true at the river-estuary interface where flocculation of organic matter acts to scavenge metals from the water column.

3. Industrialized estuaries differ from undeveloped estuaries only in the concentration of heavy metals in bottom sediments. The relative insolubility of heavy metals and the scavenging processes occurring in southeastern estuarine waters are the major reasons for this.

4. Estuaries particularly act as sinks for iron and manganese. This is probably true for other transition metals as well.

5. The accumulation of mercury in salt marsh sediments may be followed by slow release due to methylation. This results in long term, localized environmental problems related to accumulation in organisms.

6. Mercury levels in coastal littoral water vary seasonally due to seasonal atmospheric inputs. Levels vary from 0.02 to 0.3 µg/l.

7. The residence time of mercury and cadmium in coastal littoral water is estimated to be 17 and 3 weeks, respectively.

SECTION II

RECOMMENDATIONS

RECOMMENDATIONS CONCERNING CRITERIA FOR THE EVALUATION OF MAN'S IMPACT ON COASTAL LITTORAL-SALT MARSH ENVIRONMENTS.

The following recommendations relate to criteria for evaluating man's impact in coastal areas similar to the ones studied.

1. Salt marsh estuaries, because of the processes occurring there, are very vulnerable to heavy metal pollutants. In this environment, processes lead to the accumulation of heavy metals in salt marshes and increase the possibility of their entering the estuarine food web. Inputs of heavy metals by man would have far less impact if discharged to the coastal littoral environment rather than in estuarine areas. In the latter area, greater dispersion and the absence of processes bringing about accumulation, decrease the probability of accumulation of metals in the food web.

2. In river and estuarine environments monitoring of the water column tells very little about the input of heavy metals. The determination of heavy metal concentrations in sediments reveals much greater information on the extent and impact of heavy metal pollution.

3. An estimate of the potential impact of heavy metal pollution must consider the specific metal involved. In this regard it is necessary to know details about the geochemical interactions of the given metal concerned rather than considering all heavy metals together as a group.

4. In evaluating the impact of a proposed heavy metal input into an estuarine system, an estimate of the residence time of the metal in the system must be made. For example, a slow rate of input of a pollutant over a long period of time will be equivalent to a short term massive input if its residence time in the system is long (*i.e.*, the pollutant concentration in the system builds up).

5. A sediment monitoring program in estuarine areas is recommended, especially in industrialized areas.

RECOMMENDED RESEARCH

The following research recommendations are primarily addressed to the coastal littoral-salt marsh environment. The recommendations, however, have some application to other areas as well.

1. It is of primary importance in estuarine areas to obtain knowledge on the interrelationship between the water column and sediment column. Particularly more research is needed on the distribution of heavy metals in various sediment phases and on processes that affect transfer between these phases as well as

the water column. This information is particularly important in evaluating the impact of increased heavy metals in estuarine environments because it determines residence time of the metal and the quantity of the metal which enters the estuarine food web. This information is also particularly important in evaluating the effects of sediment disturbances due to man's activities in coastal areas.

2. Better models are needed for pollutant cycling in estuaries so that the environmental impact can be evaluated. These models must not be of the general type commonly discussed in the literature, but must be specific for given pollutants.

3. A good basis for evaluating analytical data on sediments is needed so that the physical characteristics of the sediment (*e. g.*, grain size) can be taken into consideration. This may require development of special chemical leaching techniques.

4. An understanding of organism-sediment relationships regarding heavy metals is needed. Research related to this is recommended.

SECTION III

INTRODUCTION

The following report is based on results of research on EPA Project No. R-800372 for the period from 1 May 1972 to 30 April 1975. The purpose of the total project was to study the transport, fate, and geochemical interaction of heavy metals (primarily mercury and cadmium) being transported into the coastal littoral-salt marsh environment of the southeastern United States coast between Georgetown, South Carolina and Jacksonville, Florida (Figure 1). The primary objectives of the project are given below:

1. Develop a data base for the concentration of heavy metals in the coastal littoral-salt marsh environment of the southeastern United States and to elucidate their variation in time and space.

2. Determine the flux of metals into and through this system, ultimately to continental shelf waters.

3. Establish the significance of salt marsh sediments as a sink for various heavy metals.

4. Elucidate the form in which metals enter the estuarine environment and changes they undergo during transport.

5. Elucidate processes, both chemical and physical, responsible for the distribution, transport and fate of heavy metals in the nearshore (coastal littoral) environment.

6. To establish the distribution of heavy metals in continental shelf waters and their variation with time and to elucidate the processes responsible for this.

7. Develop a model for the non-biological transport of heavy metals through the coastal littoral-salt marsh environment of the southeastern United States.

All of the above objectives have been met to some degree. A complete understanding of many of the problems listed in the objectives is still lacking; however, results of this study do serve as a base.

The importance of this work lies in the fact that geochemical processes control the form and quantity in which heavy metal pollutants enter estuarine-nearshore food webs subsequent to their input by man. These processes must therefore be understood if the impact of the pollution is to be predicted. By studying natural transport and geochemical processes this prediction need not be based on actual pollution case studies.

The results of this project have been reported in several journal articles and student theses. It is not feasible to review all of these studies in this report. It is therefore meant to provide a summary of the most important results. A complete list of publications, however, is given in Section X.

Figure 1. Study area showing the location of major rivers and estuaries (in outlined areas).

SECTION IV

METHODS

In this section the sampling and analytical methods used in the study are described. Details are only given for cadmium and mercury analytical techniques to allow a critical evaluation of results. For other procedures, including the analysis of other metals, references are given where details can be found. While some analytical procedures were developed under our grant, most are slight modifications of existing procedures reported in the literature.

SAMPLING PROCEDURES

Water

The quality of any analysis of water samples for heavy metals first depends on the adequacy of collection techniques in providing uncontaminated samples. Precautions necessary in sampling depend on the sampling site, platform from which samples are collected, and processing prior to storage. In general, the approach used by most water chemists calls for the use of non-metallic samplers. Non-metallic sampling bottles lowered on non-metallic hydrolines have been successfully used in some cases. However, it has been our experience that spurious, contaminated samples are collected from time to time. For the present study a non-metallic pumping system which draws water in without allowing metal surface contact was employed. The system is so constructed that water is sucked in from the sampling site by means of a teflon tube. The water enters a teflon head to which a teflon sample container is connected. The outlet to the teflon head is connected to a vacuum pump which creates the proper suction. Once the teflon bottle has been flushed and filled with the water sample it is acidified with subboiling redistilled hydrochloric acid to a pH of 2, capped and sealed in plastic bags to be returned to the laboratory. Teflon bottles are used for water sampling because of their chemical inertness which allows them to be thoroughly cleaned prior to use.

Samples for mercury are collected in a similar way; however, they are stored in stoppered pyrex flasks and acidified with sulphuric acid for storage. The use of pyrex rather than teflon is to assure that mercury is not gained or lost through sample container walls. The acid addition here for sample preservation also is the first step in the analytical procedure described below.

Sediments

Because of higher concentrations of trace metals in sediments, precautions during collection are not nearly as severe as they are for water samples. Nonetheless it is important to take as many precautions as possible to insure that samples are uncontaminated during these procedures.

In the present study all samples of marsh sediment were collected from the interiors of marsh areas, access to which was gained by helicopter. Samples were extracted from the sediment using a non-metallic PVC coring device so that the sediment never comes in contact with metal surfaces. Upon returning to the laboratory cores are extruded and sampled at intervals placing samples in teflon beakers for digestion.

To collect bottom samples either Petersen or Eckman dredges were used. Prior to sampling these devices were painted with an epoxy resin to cover all metal surfaces. Immediately after collection samples were placed in plastic bags and frozen until their return to the laboratory for analysis.

ANALYTICAL PROCEDURES (WATER SAMPLES)

Mercury

With the introduction of new long light path length flameless mercury analyzers (*e.g.*, Laboratory Data Control Mercury Monitor), sensitivities of as low as 1 ng can be obtained so that samples as small as 200 ml can be used. Because of the inexpensive nature of the equipment required and the sensitivity and ease of the analysis the following procedure (or one similar) is favored by many marine chemistry laboratories today. The apparatus used included a long path length flameless atomic absorption system having an absorption tube with quartz end windows, a peristaltic pump and a sample aeration system such as that shown in Figure 2. Samples were collected directly in 300 ml Erlenmeyer flask with ground glass stoppers. These can then be directly fitted to the closed aeration system. The initial acid addition in Step 1 of the procedure was carried out immediately after collection to preserve the sample. The precision of analyses is about $\pm$10%.

Reagents

1. Concentrated H_2SO_4.
2. Concentrated HNO_4.
3. 5% (W/V) potassium permanganate solution.
4. 5% (W/V) potassium bisulfate solution.
5. 12% (W/V) NaCl-hydroxylamine hydrogen sulfate solution.
6. 10% (W/V) $SnCl_2$ in 3.6 N H_2SO_4.

Procedure

1. 8 ml of conc. H_2SO_4 and 4 ml conc. HNO_3 were added to a 200 ml sample.
2. Sufficient 5% potassium permanganate solution was added to maintain color for 15 minutes (approximate 3 ml).
3. Sample was allowed to stand 30 minutes and then 2 ml of 12% NaCl-hydroxylamine hydrogen sulfate solution were added.
4. 10 ml of 10% $SnCl_2$ in 3.6 N H_2SO_4, were added and sample flask was immediately fitted to aeration apparatus.

5. Closed system was allowed to equilibrate and absorption was then recorded.

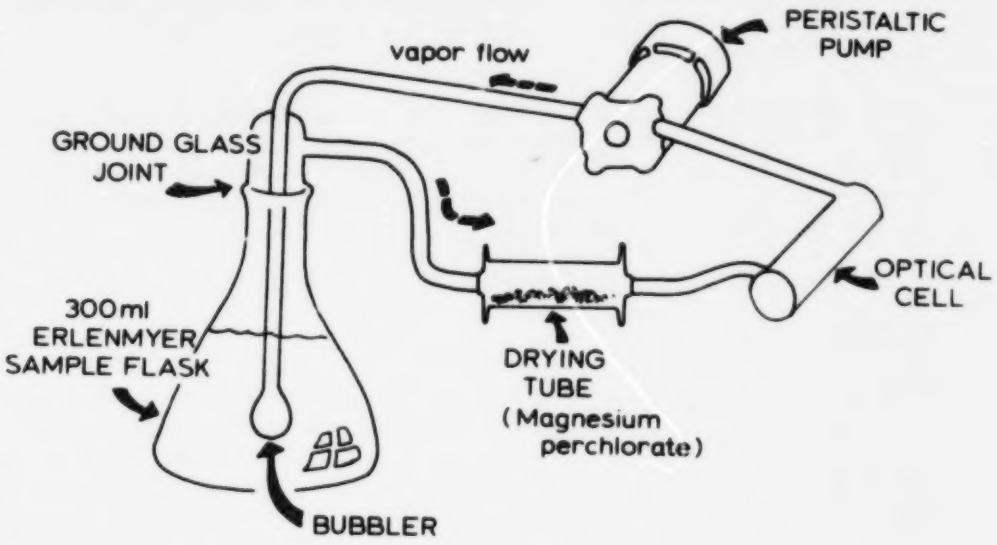

Figure 2. Schematic diagram of mercury analytical apparatus.

Cadmium

Cadmium in natural waters occurs at levels too low for direct measurement by atomic absorption spectrophotometry. Atomic absorption analyses require enrichment of the element from the original sample in order to reach concentrations above its limit of detection. Riley and Taylor (1968a) have described a method using a chelating ion exchange resin for the concentration and the subsequent determination by atomic absorption. The method is also applicable to other trace metals (Co, Mn, Ni, Zn). It involves chelating the trace metals on Chelex 100 resin and eluting them with a small volume of acid. The procedure outlined below follows that described by Riley and Taylor (1968b) with several modifications. The eluate from the column after being evaporated to dryness was dissolved in HCl rather than acetone. It was found that the addition of acetone or other miscible organic solvents produces a precipitate which clogs the aspiration assembly of the atomic absorption system. Also, if larger than 1 L samples are used, the ion exchange column should be backwashed occasionally to avoid resin compaction. A batchwise modification of this technique similar to that described by Smith (1974) alleviates many of the problems encountered with the column.

Standards were prepared by spiking water samples which had been stripped of trace metals by passage through a column of the chelating resin. A blank was prepared by processing stripped water in the absence of the spike. The absorption from the blank was subtracted from the absorption of the samples and standards. In the case of sea water this will correct for absorption due to matrix effects of samples having similar salinity (with 10°/oo). Samples differing by more than 10°/oo salinity were treated individually.

The pH of the water sample was adjusted to 7.8 ±0.1 prior to analysis. The ion exchange resin is pH selective, and the pH adjustment is critical if 100% recovery is to be obtained. The sample flow rate through the column was not allowed to exceed 5 ml/minute since the resin has a very slow exchange rate.

Replicate analyses of one large water sample indicated a precision of ±7% using this technique. As with other procedures sensitivity was improved by the application of a heated graphite furnace (Perkin Elmer HGA 2000).

Reagents

1. Chelex 100 ion exchange resin. 50-100 mesh.
2. HNO_3, (2N) (127 ml conc. HNO_3/L).
3. HCl (2N) (167 ml/L).

Procedure

1. A suitable aliquot of the resin was washed with excess 2N HNO_3 three times in (1 ml/ml of resin). Approximately 10 ml of resin were needed per column.
2. The resin was washed with double distilled H_2O and packed on an ion exchange column (1 cm diameter) to a depth of 9.0 cm. To avoid air bubbles in the resin, a few ml of double distilled H_2O was poured into the column, then the resin was poured in a thick slurry. The water level in the column was never allowed to drop below the resin bed level. This was best accomplished by connecting a piece of tygon tubing to the bottom of the column and looping it above the resin bed.
3. The ion exchange column was connected to a reservoir and the resin was washed with an additional 50 ml of H_2O.
4. The water sample, pH = 7.8, was allowed to flow through the column (5 ml/min.). The flow rate was occasionally checked with a stop watch and graduate cylinder. If more than 1 L of sample was used (usually 5L was used), the column was backwashed every two hours with distilled deionized water.
5. The column was washed with 250 ml H_2O, discarding the wash.
6. The metals were eluted with 30 ml of SN HNO_3 followed by 20 ml of 2N HCl and finally with 20 ml of double distilled water. The eluants were combined in a vycor flask.
7. The solution was evaporated to dryness at low temperature and the residue was dissolved with 1 ml of 2N HNO_3.
8. The solution was diluted to 5 ml.

Other Metals

Procedures for the analysis of other metals reported here (*e. g.*, iron and manganese) are given in either Smith and Windom (1972) or Smith (1974).

ANALYTICAL PROCEDURES (SEDIMENT SAMPLES)

Metal concentrations in sediments are much higher than those in natural waters, therefore, generally eliminating the necessity of preconcentration prior to analysis. However, other difficulties are encountered with sediment samples that are not as severe in water samples.

The greatest problem in the chemical analysis of sediments is the lack of uniformity from sample to sample. As a result samples vary in matrix composition.

For the present study atomic absorption spectrophotometric techniques emphasizing the isolation of the metal under consideration by either separation or matrix correction were used. When metals other than Hg were being analyzed, a matrix correction was used on a solution of digested sample. The sample digestion procedure for these analyses is given below followed by the mercury digestion procedure.

Procedure for Metals other than Mercury

Sediment samples are totally digested by the removal of silica. This was accomplished with hydrofluoric acid. Upon gently heating, the silica was volatilized as silicon tetrafluoride. After the complete destruction of organic matter with perchloric and nitric acids, the residue was brought into solution with 1:1 hydrochloric acid.

Digestion was carried out in teflon beakers having high acid and heat resistance. The beakers and all glassware used were cleaned in hot nitric acid and rinsed with redistilled water.

Reagents

1. Hydrofluoric acid (48%).
2. Nitric acid (conc.).
3. Perchloric acid (70%).
4. Hydrochloric acid (conc.).

Procedure

1. 0.50 gm sample was weighed onto weighing paper.
2. The bottom of a teflon beaker was covered with redistilled water. The weighed sample was dumped into the water.
3. 15 ml of HF and 10 ml conc. HNO_3 were added to each sample.
4. Samples were covered with a teflon beaker cover and allowed to stand two hours.
5. 2 ml of $HClO_4$ were added and heated on hot plate at low temperature (setting of 3) until dense fumes of perchloric acid subsided.

6. Samples were allowed to cool, and the sides of the beaker were washed with a minimum of redistilled water.
7. Samples were evaporated again to dryness.
8. The residue was dissolved with 4 ml of hot 1:1 HCl and diluted to proper volume.

Once the proper dilution of the sample was made so that the metal concentrations were in the optimum working range for atomic absorption but prior to analysis, the matrix of the sample solution was established. In the case of mercury, the problem with matrix interferences is corrected essentially by a separation technique.

Atomic absorption spectrophotometry is relatively free of interference in comparison to other spectral methods; however, interferences do exist, the most serious for heavy metals being molecular absorption. This interference is due to blocking or absorbing of some of the light passing through the flame. Calcium is probably the most serious interfering element; however, other specific element interference in trace metal analysis do occur. For cadmium these include Mg, Na, K and Fe in addition to Ca. Standard addition is not effective in dealing with this type of interference. The most effective means of dealing with the interference is by simply determining the amount of interfering elements present in the sample. When a trace blank and standards are prepared with the same concentration of interfering elements found in the sample, the interfering signal is subtracted from the total signal.

Matching sample and standard matrices of every sample was virtually impossible and unnecessary. At concentrations of the interfering element where its ratio to the concentration of cadmium was less than 500:1, the interference was almost undetectible.It was only important that sample and standard matrices did not differ by more than about 500 ppm in the concentration of the interfering element for acceptable precision. This, therefore, allowed for grouping of samples with similar matrices. Final absorption was made using a heated graphite furnace which further decreases interference.

Procedure for Mercury

A modification of the Hatch and Ott (1968) procedure was used in the mercury analysis of sediments. This procedure calls for sample (approximately 0.5 gm) digestion with a 2:1 sulphuric-nitric acid solution on a water bath at 58°C overnight. It was found that shorter digestion periods are insufficient for the complete destruction of organic matter. Samples were then transferred quantitatively to BOD bottles and brought to a volume of 200 ml with washing from the digestion beaker. The procedure at this point followed that given above for mercury in water samples.

OTHER ANALYTICAL TECHNIQUES USED IN THIS STUDY

For details of specific analytical techniques related to the characterization of organic matter and to laboratory studies the reader is directed to the references cited in subsequent sections. Because of the nature of these techniques it is unfeasible to report them here.

SECTION V

DATA BASE STORAGE

Many of the results discussed below are in a form useful to other researchers and agencies as a data base for future reference. For this reason those data that are useful in this regard and are amenable to storage are being deposited in the EPA STORET System. These are primarily water quality data that are useful independent of interpretation.

SECTION VI

HEAVY METAL TRANSPORT BY SOUTHEASTERN RIVERS

To evaluate the potential affect of increased heavy metals on the coastal littoral-salt marsh environment of the southeastern United States it is first necessary to evaluate the inputs of these metals to the system due to natural processes. Since the largest natural input of materials to salt marsh estuaries is due to river runoff, it is obvious that the quantity of metal input to this system due to this process should be ascertained. Some of the rivers in the study area are heavily industrialized. Studies of the form and concentrations of the metals in the river studied should identify characteristics of man's input. Finally the role of organic matter in the river transport of metals will enable a better understanding of the impact of this input source.

Prior to the initiation of the present study relatively little information was available on metal loads of southeastern rivers. Turekian and Scott (1967) evaluated the concentration of several heavy metals, not including mercury and cadmium, in suspended material in several southeastern streams. Windom *et al.*(1971) investigated the magnitude of the stream supply of particulate and soluble zinc, copper, cobalt, nickel and chromium by the Altamaha, Ogeechee and Satilla Rivers. The results of this study, however, were based on one set of data so that seasonal variations could not be taken into account. Other than these two studies, little additional research has been carried out in this area.

To develop a better understanding of the present rate of supply of heavy metals, especially mercury and cadmium, the major rivers emptying into this area (Figure 1) were sampled biomonthy. These rivers represent about 95% of the total runoff between Cape Romain, South Carolina and Jacksonville, Florida. The concentration of iron, manganese, cadmium and mercury were determined on each sample. In addition, other studies were conducted to elucidate the form in which the metals are transported and especially the role of organic matter in this transport.

The results of these various studies are summarized below and reference is made to the pertinent published papers and reports which give the details of the studies.

CONCENTRATIONS OF HEAVY METALS IN SOUTHEASTERN RIVERS AND THEIR RATE OF TRANSPORT.

Although relatively large variations in the concentrations of the metals studied are observed for each river (Table 1) the mean concentration of cadmium and mercury differ little between rivers. Iron and manganese, however show relatively high variability. This may reflect variations in the composition of the drainage basins for each river as does the mineralogical composition of suspended matter (Neiheisel and Weaver, 1967; Windom, *et al.*, 1971).

Like the dissolved metal loads the concentration of mercury and cadmium in particulate matter also varies little from river to river with larger variations in iron and manganese (Table 2). Again this probably reflects drainage basin composition.

Table 1

MEAN AND RANGE IN DISSOLVED METAL CONCENTRATIONS IN SOUTHEASTERN RIVERS[1]

River		ppb Fe	Mn	Cd	Hg
Pee Dee	Mean	210	21	1.0	0.06
	Max	450	40	1.4	0.10
	Min	90	12	0.4	0.02
Black	Mean	240	18	1.0	0.06
	Max	410	53	3.6	0.14
	Min	60	8	0.1	0.02
Santee	Mean	170	12	0.4	0.05
	Max	360	53	0.7	0.08
	Min	30	3	0.1	0.02
Cooper	Mean	80	3	0.7	0.04
	Max	240	8	2.6	0.08
	Min	10	1	0.1	0.02
Savannah	Mean	170	21	0.3	0.07
	Max	380	34	0.6	0.13
	Min	70	6	0.2	0.02
Ogeechee	Mean	310	33	1.0	0.07
	Max	490	63	2.0	0.14
	Min	140	15	0.4	0.02
Altamaha	Mean	150	17	0.8	0.05
	Max	280	39	2.6	0.06
	Min	30	2	0.2	0.02
Satilla	Mean	370	42	0.8	0.07
	Max	610	85	1.6	0.14
	Min	280	22	0.3	0.04
St. Johns	Mean	70	4	0.8	0.05
	Max	90	8	1.5	0.08
	Min	40	2	0.1	0.03

[1]Based on results of a total of from 6 to 30 samples collected from each river bimonthly, May 1972 to July 1973.

Table 2

AVERAGE METAL CONCENTRATION IN SUSPENDED SEDIMENT OF SOUTHEASTERN RIVERS[1]

River	Av. Suspended Sediment Load (mg/l)	ppm			
		Fe %	Mn	Cd	Hg
Pee Dee	9	6.6	1050	5	0.5
Black	11	5.0	1490	7	0.6
Santee	53	5.7	1400	3	0.2
Cooper	7	5.7	830	15	1.0
Savannah	22	8.2	1120	8	0.7
Ogeechee	7	5.0	1300	13	0.6
Altamaha	16	5.2	1600	26	0.7
Satilla	26	6.2	330	10	0.4
St. Johns	12	4.4	500	20	0.6

[1]Based on results of a total of from 6 to 30 samples collected from each river bimonthly, May 1972 to July 1973.

Three of the rivers studied (Savannah, Cooper and St. Johns) are highly industrialized and are expected to receive large concentrations of heavy metal pollutants. The lack of significantly increased levels of the metals studied in these rivers, however, indicates that the increased industrialization is not reflected in water column concentrations. Because of the short residence time of heavy metals in natural waters, it is more likely that they accumulate in bottom sediments shortly after their input from industrial effluents. Subsequent transport in the river is probably then by bedload traction.

Present rates of input of iron, manganese, cadmium and mercury to the southeastern coastal littoral-salt marsh environment by rivers can be estimated from the concentration of metals in both dissolved and particulate forms and the average annual discharge of each river.

These results (Table 3) indicate that most of the iron that is carried by rivers is in particulate form, while a relatively small percentage of the cadmium and mercury is particulate. Manganese is equally distributed between the two phases. A detailed analysis of particulate matter in the Savannah and Ogeechee Rivers for trace metal partitioning between phases (*i.e.*, absorbed, reduced, oxidized and residual) indicates that most of the iron is in refractory residual phases. Manganese occurs in reduced phases with significant amounts adsorbed and in residual phases. Cadmium shows the highest concentration in residual and reduced phases.

The details of the research described in this section are given in Windom (1975). Results of studies on metal partitioning in particulate matter are given in Nance (1974).

HEAVY METAL-ORGANIC MATTER INTERACTIONS IN SOUTHEASTERN RIVERS

As a part of this project studies of the composition of southeastern river water organic matter was determined and its interaction with heavy metals was investigated. The results of these studies are given in Beck *et al.*, (1974), Dunn (1974) and Martin (1973).

The chemical characteristics of southeastern rivers, especially those whose drainage basin is entirely in the coastal plain, differ considerably from those of most rivers of the world (Beck *et al.*, 1974). The difference is reflected primarily in the dominance of organic matter over inorganic constituents and the resultant low pH. Based on chemical and physical characteristics, southeastern river water organic matter consists of humic substances, the bulk of which resembles fulvic acid. In areas of high rainfall, and low relief such as Coastal Plain River Basins, large quantities of humic substances are produced from the degradation of abundant vegetative litter (Beck *et al.*, 1974). Of the humic substances produced, only the more soluble, lower molecular weight material is carried into the river. Limited by its solubility in water, river water organic matter is of relatively low polydispersity when compared to other humic substances (Martin, 1973). As river water organic matter is transported downstream, the higher molecular weight portion (low in total acidity) resembling humic acid is removed, probably by flocculation. The dissolved organic matter transported to the estuary would be characterized by low molecular weight and high exchange capacity.

The importance of humic materials as complexing agents in soils has been studied by numerous experimenters (see Schnitzer and Kahn, 1972, for a review). Beck *et al.*, (1974) considered the possible role of river water organic material in mobilizing complexed metals in natural waters. These organic compounds can effectively increase the solubility of metals and retard precipitation (Rashid *et al.*, 1973), providing a mechanism for heavy metal transport and enrichment. As a part of this research program an examination was made

Table 3

METAL TRANSPORT BY SOUTHEASTERN RIVERS

	Average Annual Discharge (10^{12}l)	Annual Metal Transport (10^6 Kg) Fe		Annual Metal Transport (10^3Kg) Mn		Cd		Hg	
		D	P	D	P	D	P	D	P
Pee Dee	11.7	2.5	7.0	240	110	11.4	0.6	0.64	0.06
Black	0.8	0.2	0.5	14	13	0.9	0.1	0.09	0.01
Santee	1.9	0.4	5.6	20	140	0.7	0.3	0.08	0.02
Cooper	12.7	1.0	5.1	41	74	8.6	1.4	0.52	0.08
Savannah	10.4	1.9	18.7	230	250	3.2	1.8	0.65	0.15
Ogeechee	2.0	0.6	0.7	66	18	1.8	0.2	0.09	0.01
Altamaha	11.9	1.8	9.5	195	305	9.1	4.9	0.58	0.12
Satilla	2.0	0.8	3.1	83	17	1.5	0.5	0.18	0.02
St. Johns	5.0	0.3	2.5	20	30	3.8	1.2	0.26	0.04
Total	58.4	9.5	52.7	909	957	41.0	11.0	3.09	0.51
Grand Total		62.2		1866		52.0		3.60	
Percent Particulate		85		51		21		14	

of the mechanism and degree of transport of purified river water organic-cadmium complexes to enable a more complete assessment of the possible impact of the mobilization of toxic metals in marine environments (Dunn, 1974).

A sample of dissolved river water organic acid (largely fulvic acid) was extracted from the Satilla River and purified. Cd-organic acid complexing studies were performed using potentiometric titrations, with and without a background of Cd^{2+}. Acid dissociation values were obtained from the acid-base titration data using the assumption of the similarity of the system to a polyprotic acid, and Cd-organic stability constants were obtained from titrations with a background of Cd in which the free cadmium ion was followed with a Cd electrode. Results indicate that the nonchelating complexing phenomenon can play an important part at low pH and can explain the change in stability constants with pH noted by other experimenters. At pH 6.3 Cd-organic complexes form in a 1:1 ratio of chelated to non-chelated complexes. At lower pH levels non-chelated complexes become increasingly important, a result which is of direct interest to those concerned about the environmental impact of the mobilization of toxic metals.

The results of these studies have broad implications regarding environmental problems such as the toxic metal pollution of rivers and estuaries. Heavy metal pollutants have the ability to form stable, water soluble organo-metallic complexes with humic substances (Schnitzer, 1971). Precipitation of heavy metals as insoluble salts is prevented by the presence of soluble humic substances (Rashid and Leonard, 1973).

In the Satilla River and other rivers, where dissolved organic matter resembling humic substances is abundant, its presence may play an important role in the transportation of heavy metals. Organic matter and metal-organic complexes are introduced to the estuary as either dissolved or colloidal material. In laboratory studies, the addition of an electrolyte such as NaCl to humic colloids causes coagulation (Ong and Bisque, 1968). Thus it is expected that when soluble organic matter and associated metals transported by river water encounter increased salinity in the estuary, flocculation occurs resulting in rapid deposition and accumulation of metal in salt marsh sediments.

SECTION VII

HEAVY METAL GEOCHEMICAL INTERACTIONS IN ESTUARIES

One of the prime objectives of this study was to evaluate geochemical interactions involving heavy metals entering estuaries in river runoff. This information is of primary importance in evaluating the environmental impact of heavy metal inputs to the coastal littoral-salt marsh system. By understanding these processes it is possible to predict whether a given metal will accumulate in salt marsh estuaries or be transported directly to the coastal littoral environment. This obviously determines the point of impact.

The geochemical processes affecting heavy metal fate in estuaries are schematically shown in Figure 3. In this model the river is divided into three compartments or phases which contain metals. As river water is transported into estuaries metals are potentially transferred from one compartment of the river system to various compartments or phases of the estuarine water column as indicated (processes 1 through 9). Once the metals are in the estuarine system in one of the various compartments, their fate there depends on the transfer to other compartments where modifications may occur to produce further transfer. Ultimately the metals must be transferred out of the estuarine system by various pathways, the importance of which depends upon the coefficient of transfer. In the present model only the non-biologic part of the system is considered; therefore, only two pathways of loss can be identified. These are (1) loss to the marsh sediment due to sediment accumulation which is assigned the transfer coefficient K_{15} and (2) loss in solution due to offshore transport (transfer coefficient K_{16}). It is obvious that the offshore transport of metals could be in the tissues of migrating organisms or rafted marsh grass detritus. For the present simplified model which considers only geochemical processes however, the form in which the metal is transported out of the system is not important.

The model in Figure 3 emphasizes the geochemical processes that are of interest. Generally they can be divided into two categories. The first includes those occurring at the salt water-fresh water boundary. The second includes processes occurring in the estuary itself. Within each of these categories specific important processes or process related phenomena were studied. These are listed immediately below with specific references to a more complete discussion and are summarized in the following paragraphs of this section.

Geochemical processes occurring at the river-estuary boundary.

1) Metal concentration variations in solution versus salinity (Windom, 1975).
2) Adsorption-desorption reactions (Nance, 1975).
3) Variations in metal partitioning in particulate matter in rivers versus estuaries (Nance, 1974).
4) Flocculation at the river-estuary boundary (Arnone, 1974).

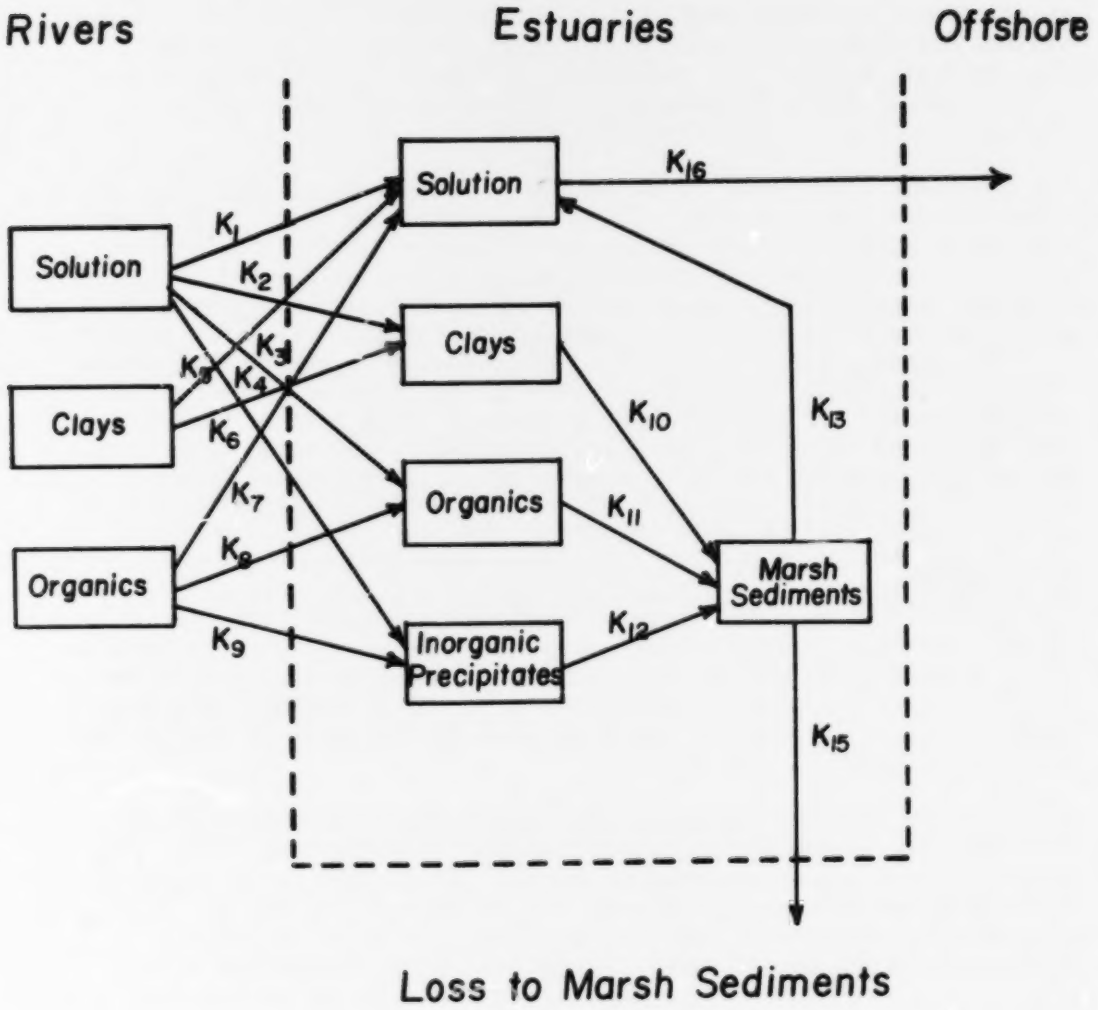

Figure 3. Schematic non-biologic model for pollutant transfer through estuaries.

Geochemical processes occurring in estuaries.

1) Characteristics of heavy metal accumulation in salt marsh sediments (Windom, 1974).
2) Remobilization of mercury from sediments due to methylation (Windom *et al.*, 1975).

METAL CONCENTRATION VARIATIONS IN SOLUTION VERSUS SALINITY

Concentrations of heavy metals in rivers are generally much higher than those found in marine waters (Turekian, 1971). Even coastal waters of the southeastern United States show levels of metals higher than those of the open ocean indicating an increasing concentration gradient from offshore to inshore (Windom and Smith, 1972). If metals transported in solution by rivers undergo no reaction that lead to their precipitation in the estuarine zone (*i. e.*, conservative mixing), variations in their concentrations would be a linear function of salinity, showing a decrease due to dilution with metal poor marine waters. If, on the other hand, the metal concentrations change with salinity in a nonlinear way, the influence of processes other than dilution is indicated.

The variations in metal concentration with salinity in eight southeastern estuaries (Figure 1) were determined and exhibited expected characteristics. For example, iron decreases exponentially with increasing salinity (Figure 4) owing to its precipitation upon entry into the estuarine zone. Manganese shows a similar but less pronounced trend. These decreases in iron and manganese at the river-estuary boundary may be due to the formation of hydrated iron oxide which flocculates, precipitates and accumulates in estuarine sediments. The increased electrolyte concentration of estuarine waters can also influence the fate of very fine (<0.45 microns) particulate iron and manganese associated with organic matter, also leading to their flocculation. Variations in Cd and Hg with salinity (Figure 5) appear to follow what is expected for more conservative mixing, in that significant changes in concentrations from rivers to estuaries are not observed.

These results imply that estuaries are sinks for dissolved riverborne iron and manganese but not cadmium and mercury. The solubility of the forms of these latter two metals in rivers is apparently not greatly different than that in estuarine waters. This is clearly not the case for iron and manganese. Since iron precipitation is an effective means of scavenging other heavy metals, especially those in the transition series, its accumulation in estuaries may be accompanied by the accumulation of other metals. As is the case in fresh water, cadmium and mercury inputs by man would not be reflected in the estuarine water either.

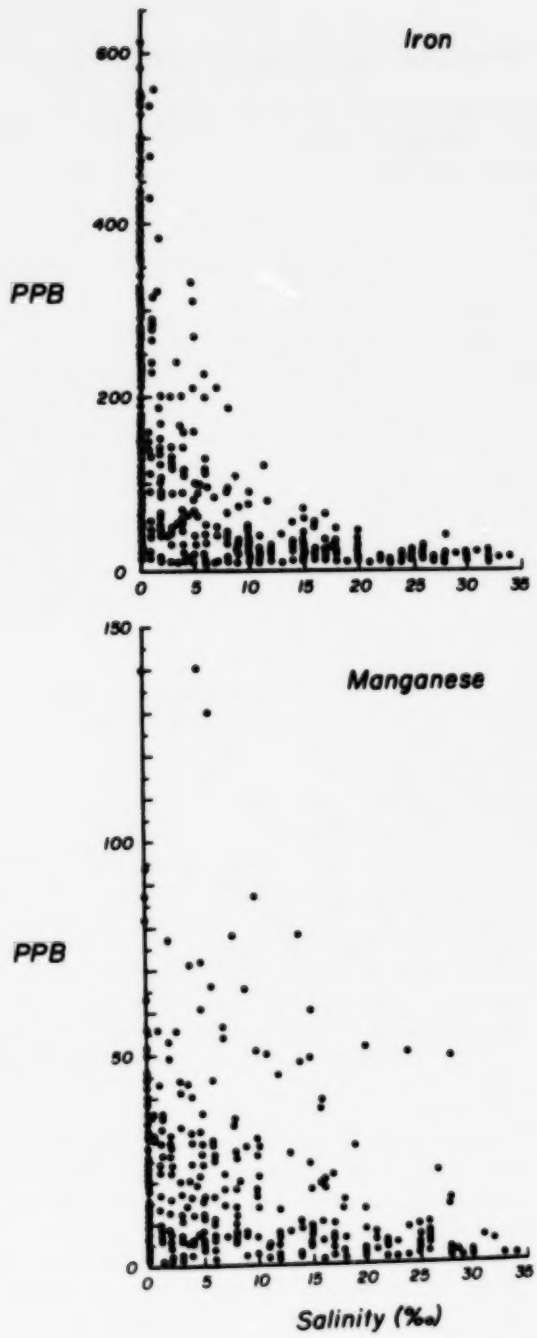

Figure 4. Iron and manganese concentrations in estuarine waters versus salinity.

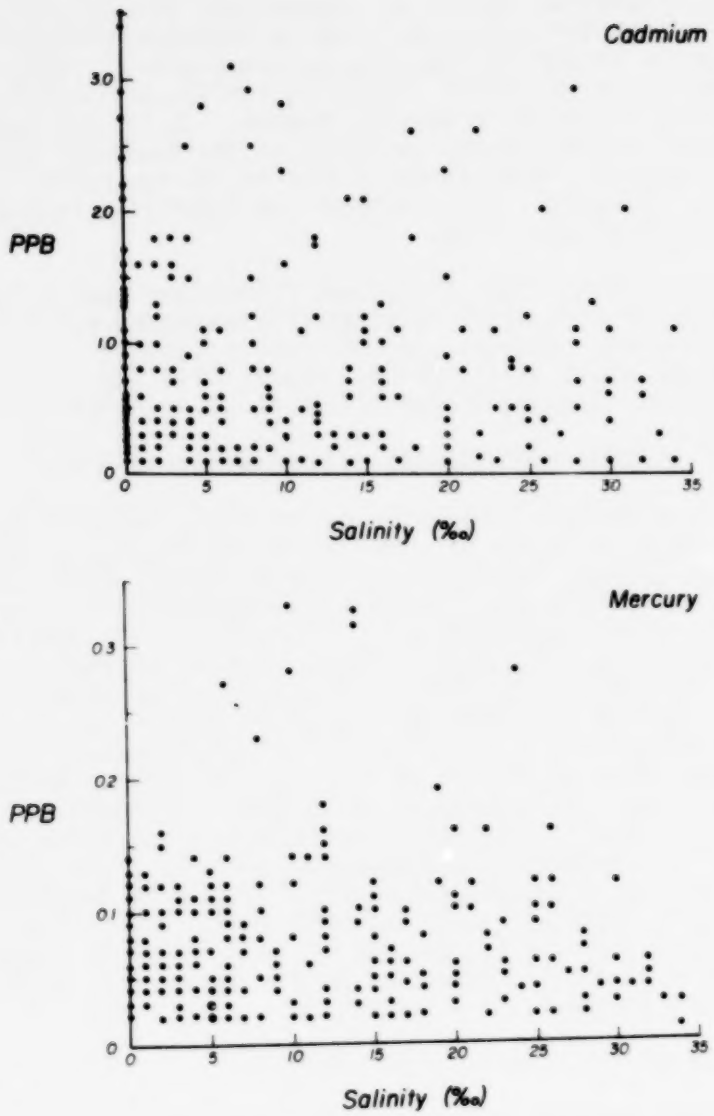

Figure 5. Mercury and cadmium concentrations in estuarine water versus salinity.

ADSORPTION-DESORPTION REACTIONS

As suspended matter moves across a salinity gradient the increased ion strength of estuarine waters is probably the major factor in adsorption-desorption reactions. Common ions such as Na+, K+, Ca++ and Mg++ compete for adsorption sites on suspended sediment, hence decreasing its adsorption capacity for trace metals. This adsorption-desorption mechanism probably functions for Zn, Cd, and Mn in southeastern river estuaries to varying degrees. It is also apparent that seasonal changes in the character of the suspended sediment (primarily organic matter content) affects its adsorption capacity for Cd, Mn, Zn and Hg. These changes are especially important in the uptake and release of Hg.

Radioisotopes (^{65}Zn, ^{54}Mn, ^{109}Cd, and ^{203}Hg) were used to trace the effect of salinity on metal exchange with suspended sediment in southeastern estuaries. Results indicate that a substantial release of Cd, Zn and Mn occurs at salinities between 0°/oo and 5°/oo. No direct correlation was observed between salinity and Hg exchange.

VARIATIONS IN METAL PARTITIONING IN PARTICULATE MATTER

Suspended sediment collected from the estuarine zones of two major southeast Georgia rivers (Savannah and Ogeechee) were analyzed using a selective chemical leaching technique to determine the role of suspended material on metal transport in southeastern estuarine environments. The metal concentrations (Cu, Cd, Pb, Zn, Mn, and Fe) in the leached fractions, (adsorbed, reduced, oxidized and residual) of suspended sediments from fresh water and saline environments were compared. Results indicate that suspended sediment can account for a significant portion of these metals in natural waters. Generally, the residual fraction (metals in lattice sites of crystalline detrital material) and the reduced fraction (metals precipitated and coprecipitated as metallic coatings) are the phases containing the major portion of the trace metals in suspended sediment. The effect of salinity changes on the metal concentrations of the leached fractions appear to be a function of the specific metal, season, and area of study. Comparison with the results of similar studies indicate the importance of regional differences in the character of suspended matter on the transport of trace metals.

FLOCCULATION AT THE RIVER-ESTUARY BOUNDARY

At the initial appearance of salt water (3-50 ppm Na) organic-rich floccules occur which are not observed upstream in coastal plain rivers such as the Satilla. The organic carbon content of the floccules decreases with increasing salinity (>50 ppm Na). Dissolved organic carbon (DOC) decreases proportional to the mixing with sea water. Therefore, the organic floccules do not appear to originate immediately by precipitation of the DOC, and thus the composition of the floccules is not quite understood. The suspended particulate organic carbon (POC) appears to be incorporated with the resuspended bank material in the mixing zone and eventually becomes included in the marshes.

Dissolved metals show a rapid decrease seaward and are assumed to be incorporated into the floccules. However, the increase of metals in suspended particulate matter observed in the mixing zone is not attributed to this incorporation only. An increase in the concentration of the suspended material in the mixing zone due to resuspension of bank material is related to the increase of metals in the particulate matter and masks the precipitational feature of the dissolved metals.

CHARACTERISTICS OF HEAVY METAL ACCUMULATION IN SALT MARSH SEDIMENTS

The Fe, Mn, Cu, Cd, Hg, Pb and Zn concentrations were determined at 10 cm intervals on cores taken from 25 stations in salt marshes (Figure 6). Throughout this area the average concentration of the metals (Table 4) appears to be relatively constant. The small variations that are present are probably due to variations in organic matter as appears to be the case for mercury (Figure 7). No differences due to geographical area were indicated in these results.

The overall mean concentrations of heavy metals in salt marsh sediments can be taken to represent what metal levels unpolluted sediments in the coastal littoral-salt marsh environment should be. The concentrations of heavy metals in the sediments of three major harbors in the study area (Charleston, South Carolina, Savannah and Brunswick, Georgia) are generally higher than these levels. For example, the average concentrations of mercury, cadmium, lead and zinc in Charleston Harbor sediments are over twice that of the average salt marsh. This is the worst case observed in the area studied.

By using an average sediment accumulation rate of 1 mm/yr for salt marsh sediments as explained in Windom (1975), the rate of accumulation of heavy metals can be estimated. These are given in Table 4. Applying these values to the total 400 hectare salt marsh system a budget can be established for Fe, Mn, Cd and Hg since their river inputs are known (Table 5). From this budget it can be seen that salt marshes act as a sink for Fe and Mn while only the particulate Cd and Hg accumulates there.

REMOBILIZATION OF MERCURY FROM MARSH SEDIMENTS DUE TO METHYLATION

During the course of this study, an area highly contaminated by mercury inputs from a chloralkali plant was investigated. The source of the mercury has been previously identified by EPA as the Allied Chemical Company near Brunswick, Georgia (Figure 8). Although the mercury input occurred over several years, its impact apparently has only been on a local area judging from the Hg concentration in sediments (Table 6). The discharge was discontinued in 1972; however, high levels of mercury are still present.

The initial input of the inorganic mercury would be followed by accumulation in adjacent sediments, therefore affecting only a localized area. One of the important processes for subsequent remobilization of the mercury is methylation in the sediment column. Using data on the accumulation of methylmercury in lower trophic level organisms from this area, Windom *et al.* (1975) estimated the annual production rate

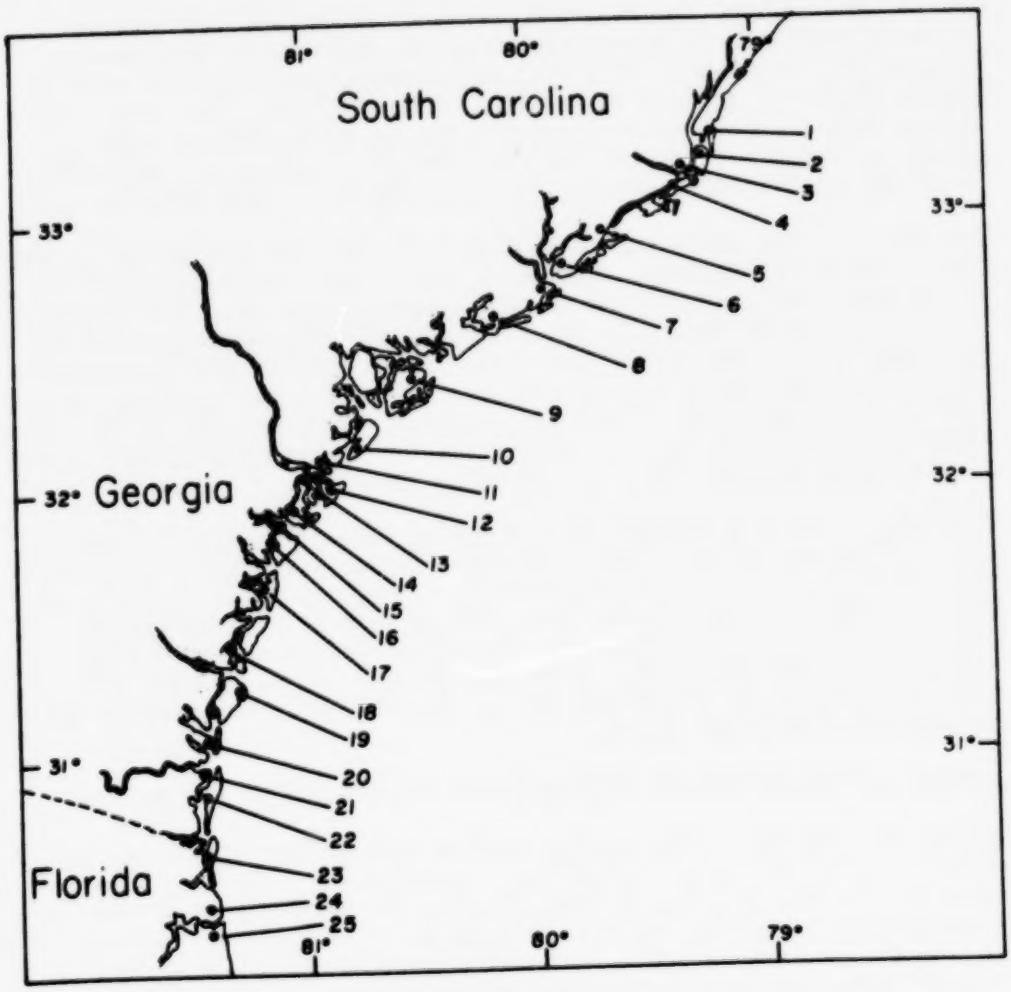

Figure 6. Salt marsh core locations.

Table 4

AVERAGE METAL CONCENTRATIONS IN MARSH CORES

(Dry Weight Basis)

Station Number	% Fe	ppm Mn	Cu	Hg	Cd	Pb	Zn
1	3.9	103	30	0.12	3.4	25	63
2		250	16	0.09	5.0	26	67
3	3.9	166	26	0.16	2.9	20	67
4	5.0	142	25	0.05	3.3	20	72
5		209	24	0.08	4.4	27	70
6		158	10	0.01	1.0	16	36
7	1.2	139	4	0.04	0.4	9	51
8	1.8	114	4	0.02	0.8	9	21
9	4.1	309	16	0.04	2.1	13	51
10	1.9	174	3	0.04	0.1	4	11
11	2.4	151	8	0.06	0.5	8	67
12	4.8	260	12	0.09	0.6	16	70
13	4.6	353	20	0.16	0.8	21	81
14	3.4	319	10	0.10	0.4	20	57
15	4.0	173	10	0.11	018	19	64
16	2.9	366	8	0.02	0.8	15	48
17	2.7	262	6	0.05	0.2	20	42
18	3.2	273	12	0.16	0.8	24	61
19	1.1	175	4	0.03	1.6	11	17
20	3.7	168	8	0.06	0.8	15	43
21	3.1	244	8	0.07	1.2	12	37
22	4.7	132	7	0.06	0.8	13	39
23	2.9	128	10	0.08	0.7	20	45
24	0.9	205	5	0.05	0.8	15	21
25	1.5	74	2	0.05	0.4	9	15
Mean	3.1	202	11	0.07	1.4	17	49
Average Accumulation Rate* ($mg/m^2 \cdot yr$)	4.5×10^4	303	16	10	2.1	25	71

*Assuming an average sedimentation rate of 1 mm/yr and an average specific gravity of marsh sediments of 1.5 g/cc.

Analytical techniques similar to those for suspended sediment.

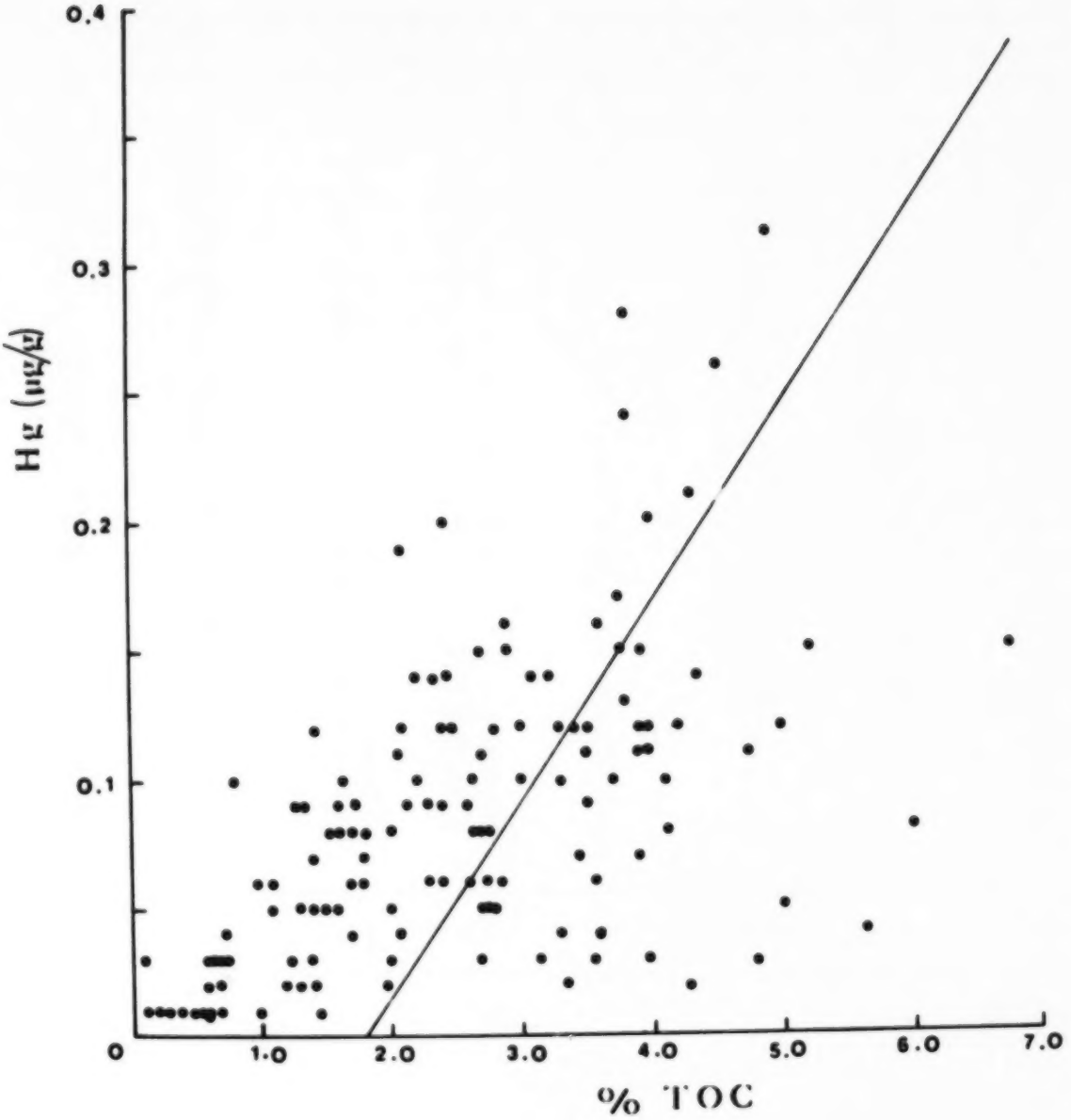

Figure 7. Mercury concentration in marsh sediments versus total organic carbon (regression line drawn through data).

Table 5

BUDGET FOR THE ANNUAL FLUX OF METALS THROUGH SOUTHEASTERN ATLANTIC SALT MARSH ESTUARIES

	Fe (10^6Kg)	Mn	Cd (10^3Kg)	Hg
Total Input	62	1866	52	3.6
(% of total input in particulate phases)	(85)	(51)	(21)	(14)
Sedimentation Loss	210	1200	9	0.4
% Sedimentation Loss	100	64	17	11
Net Flux through Estuary	0	666	43	3.2

Table 6

CONCENTRATION OF MERCURY IN MARSH SEDIMENT

Station Number	Total Hg (ppm dry wt.) 0 - 5 cm	5 - 10 cm
1	1.34	0.15
2	0.34	0.08
3	---	0.06
4	1.70	0.48
5	0.48	0.33
6	0.27	0.08
7	0.55	0.82
8	0.41	0.30
9	0.28	0.25
10	0.27	0.23

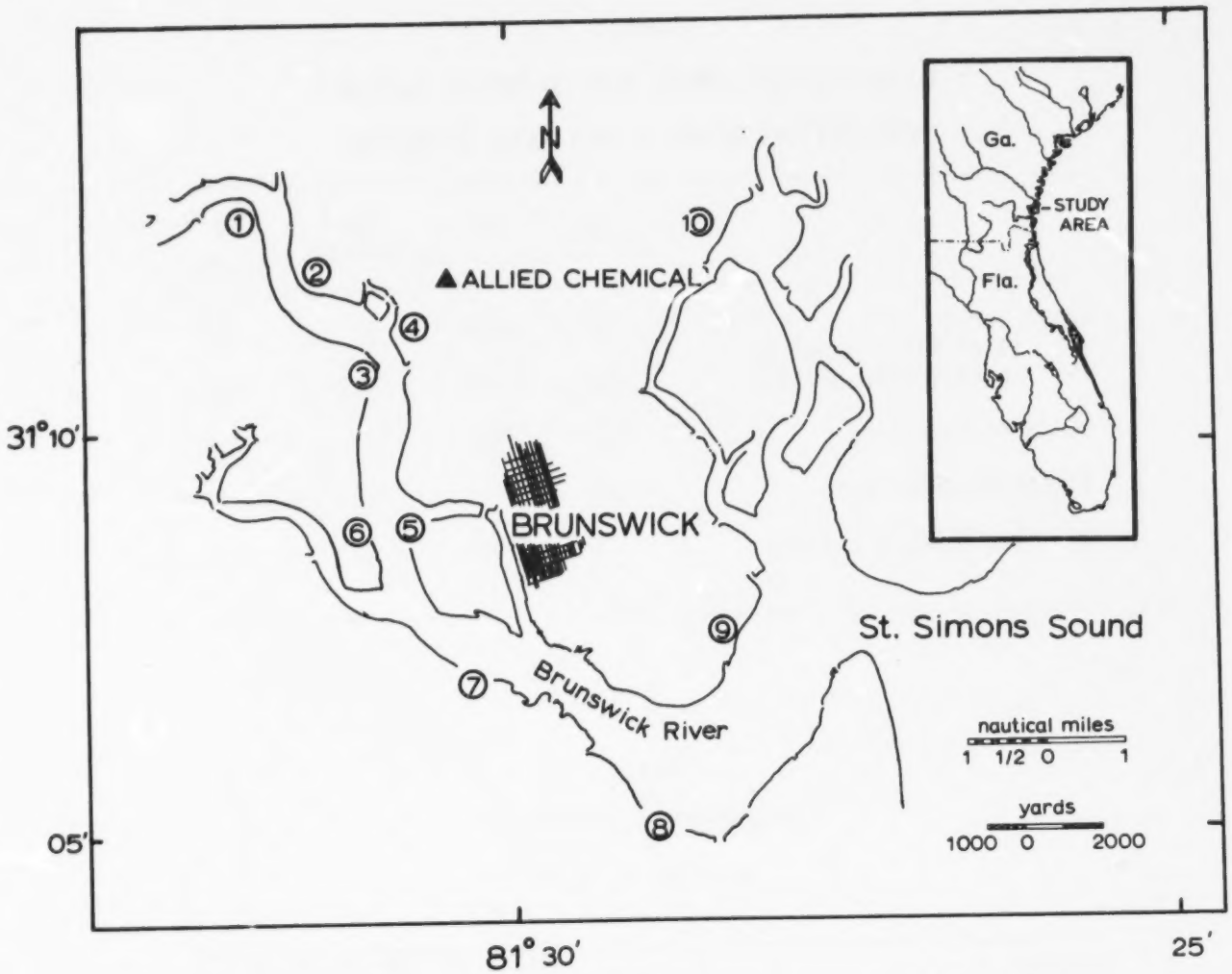

Figure 8. Station location in vicinity of mercury contaminated study area.

of this form to be approximately 50 µg/g of total mercury in the upper 5 cm of the marsh sediment column. From these results it would appear that the loss of mercury from the system might be a slow process. In fact, the Department of Natural Resources for the State of Georgia has reported high levels of mercury in a number of game animals from this areas over the last several years. Results of the present study suggest that this may persist for some time to come.

SECTION VIII

CADMIUM AND MERCURY IN COASTAL LITTORAL WATERS

The coastal littoral environment extends offshore to less than 20 km. The average water depth is about 5 m and the length of the system between Cape Romain, South Carolina and Jacksonville, Florida is approximately 300 km. This environment receives inputs of metals from the adjacent southeastern United States and under steady state conditions the concentration of a given metal will depend on its rate and mode of input and its residence time in the environment. This latter parameter is primarily influenced by water mass mixing and exchange. To predict the impact of increased metal inputs on coastal littoral waters, information on the above parameters is critical. This is especially true if the input occurs directly to the coastal littoral environment. The input due to rivers would, to a large degree, be controlled by processes occurring in estuaries which would tend to act as buffers.

The following paragraphs summarize data obtained on the rate of input, concentration and residence time of cadmium and mercury in the southeastern coastal littoral environment.

MERCURY CONCENTRATION IN, AND INPUT TO, COASTAL LITTORAL WATERS

Windom *et al.* (1975) found that the mercury concentration in continental shelf waters, including those of the coastal littoral environment, vary seasonally, ranging from a minimum of 5 ng/l to a maximum of 300 ng/l. These variations cannot be explained by river runoff. Studies of the concentration of mercury in the atmosphere, however, suggest that atmospheric transport may provide a major input. This conclusion is based specifically on the observation that mercury in the atmosphere is highest during periods of offshore winds and this is correlated to high mercury concentrations in the water column. It is estimated that the annual input of mercury to these waters due to atmospheric transport is greater than .3 mg/m^2. Added to the net flux through estuaries due to runoff, the total mercury input to the coastal littoral environment is approximately 5.4 metric tons per year.

Taken over the entire year the average concentration of mercury in coastal littoral waters is approximately 60 ng/l. Judging from the relatively rapid fluctuation of mercury in these waters, physical processes of mixing must occur within a relatively short time period.

CADMIUM CONCENTRATION IN, AND INPUT TO, COASTAL LITTORAL WATERS

The average concentration of cadmium in coastal littoral waters has been reported to be approximately 0.1 µg/l (Windom and Smith, 1972). This concentration is somewhat higher than those found offshore and indicates an effect due to coastal runoff.

The annual input of cadmium to estuaries due to river runoff was discussed in Section VI. Only a portion of this, however, ultimately reaches the coastal littoral environment as is indicated in Table 5. Using the results shown in this table the annual input of cadmium is estimated at 52 metric tons.

RESIDENCE TIME OF MERCURY AND CADMIUM IN COASTAL LITTORAL WATERS

The residence time of a metal in coastal littoral waters can be expressed by the following equation:

$$T = \frac{C}{dc/dt}$$

Where C is the total content of the metal in coastal littoral waters and dc/dt represents its rate of input. If it is assumed that the rate of mixing of continental shelf waters is relatively constant, then the concentration of a given heavy metal in the coastal littoral waters would be a function of input rate (steady state). Therefore, if the residence time of the metal in these waters is known then the concentration of the metal can be predicted for increased rates of input.

The approximate volume for coastal littoral waters is 3×10^{10} cubic meters. Using this volume and the concentration of mercury in Windom *et al.* (1975), the total content of the these two metals in coastal littoral waters can be determined (Table 7). Using the annual inputs of these two metals, their residence times can be estimated (Table 7). The residence times calculated for the two metals appears to be similar to the mixing time expected for the area.

Table 7

RESIDENCE TIME OF MERCURY AND CADMIUM

IN COASTAL LITTORAL WATERS

	Content of Coastal Littoral Waters (in metric tons)	Annual Input (metric ton/yr)	Residence Time (weeks)
Mercury	1.8	54	17
Cadmium	3.0	52	3

SECTION IX

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SECTION X

PUBLICATIONS

The following is a list of publications which cite the support of EPA Grant No. R800372.

1973 Bloomer, D.R., A hydrographic investigation of Winyah Bay, South Carolina and the adjacent coastal waters, M.S. Thesis, Georgia Institute of Technology, Atlanta, 57 pp.

1973 Martin, S.J., Chemical characteristics of dissolved organic matter in river water, M.S. Thesis, Georgia Institute of Technology, Atlanta, 45 pp.

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1974 Beck, K.C., Renter, J.H. and Perdue, E.M., Organic and inorganic geochemistry of some coastal plain rivers of the Southeastern United States, Geochim. Cosmochim, Acta, 38, 341-364.

1974 Dunn, T.H., Electrode studies of stability constants of Cd-river water organic matter complexes, M.S. Thesis, Georgia Institute of Technology, Atlanta, 70 pp.

1974 Nance, S.W., The role of suspended matter on trace metal transport in an estuarine environment, M.S. Thesis, Georgia Institute of Technology, Atlanta, 36 pp.

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